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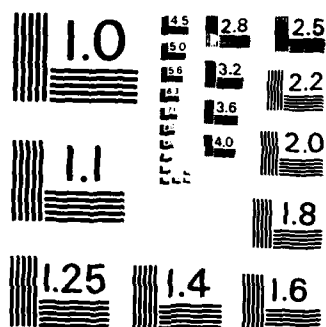
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MEASUREMENT OF LIFETIMES OF THE VIBRATIONAL LEVELS
OF THE B STATE OF N_2

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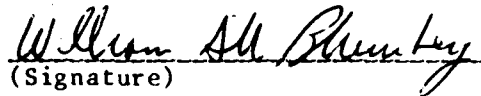
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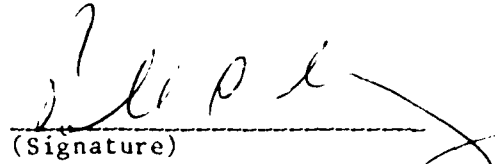
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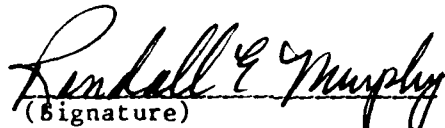

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1.0 Abstract

This report summarizes two series of investigations of molecular nitrogen. In the first series of experiments the lifetimes of selected levels of the $B^3\Pi_g$ state of N_2 were measured. A chopped cw dye laser beam was employed to excite selected levels of the $B^3\Pi_g$ state of N_2 in a beam of molecules in the $A^3\Sigma_u^+$ metastable state. Laser induced fluorescence was observed from the vibrational levels $v=5$ through $v=12$, and a photomultiplier was used in conjunction with a microcomputer system to measure the time dependence of the decay light. The lifetimes which were measured to an accuracy of 3% showed a smooth decline from 5.8 μsec for $v=5$ to 4.11 μsec for $v=12$. No dependence on rotational level was observed. In the second series of experiments an attempt was made to produce a beam of metastable N_2 molecules in the $a''^1\Sigma_g^+$ state, use a dye laser to excite them to the $c_4(0)^1\Pi_u$ and $(c'_5(0)^1\Sigma_u^+)$ metastable states, and observe the fluorescent radiation.

$c_4(0)^1\Pi_u$

$c'_5(0)^1\Sigma_u^+$

$a''^1\Sigma_g^+$

2.0 Introduction

The work under this contract is divided into two separate tasks. The first task was to measure the lifetimes of vibrational levels belonging to the $B^3\Pi_g$ state of molecular nitrogen. The second task was to perform exploratory experiments using the laser-molecular beam method to study the higher Rydberg states of molecular nitrogen employing the $a''^1\Sigma_g^+$ and $E^3\Sigma_g^+$ metastable states as entry levels for excitation of higher Rydberg states. In this report we will treat these two tasks separately and deal with them in the same order in which they were carried out.

3.0 Lifetimes of $B^3\Pi_g$ Levels of N_2

3.1 Motivation

The first positive system of N_2 , which arises from radiative transitions between the $B^3\Pi_g$ and the $A^3\Sigma_u^+$ states is one of the strongest components of the emission spectrum of excited N_2 . Accurate values of the lifetimes of the B state vibrational levels and the radiative rates for the $B \rightarrow A$ transitions are required to understand the dynamics of the relaxation of a population of excited nitrogen molecules. These lifetimes and transition rate data are also an important ingredient for understanding and modeling the time dependence of the radiance of the disturbed atmosphere.

Because of their importance, many experiments¹⁻⁷ have been carried out to measure the lifetimes of the $B^3\Pi_g$ state of N_2 . Several techniques were used and the results from the different experiments disagreed con-

siderably and made it difficult to know which values for the lifetime to believe. Table I summarizes all the measurements that had been carried out prior to those reported here together with the results for this experiment. It was the purpose of the present work to measure the lifetimes of many different vibrational levels of the B state with a precision of 5% or better to clarify the situation.

3.2 Method

For the measurement of these lifetimes we used a laser spectroscopy-molecular beam technique. Figure 1 shows a schematic drawing of the apparatus. A crossed electron beam was used to excite nitrogen molecules from the ground state up into the $A^3\Sigma_u^+$ metastable state. The beam from a dye laser was used to excite the metastable molecules up into selected levels of the $B^3\Pi_g$ state and the laser radiation was observed with a cooled photomultiplier tube. To measure the lifetimes, an optoacoustic modulator was employed to pulse the light and the lifetimes were determined from the decay time for the fluorescent radiation. This technique provides selective excitation and is free of the systematic errors due to cascades from higher states which plagued many of the other measurements in which a pulsed electron beam was used to excite N_2 molecules up to the $B^3\Pi_g$ state.

3.3 Apparatus

The apparatus used for this work is similar to an arrangement used previously to measure the lifetimes of some $n=3$ states in H_2 . A molecular beam is formed by effusion through a narrow slit, and a fraction of the beam is excited by electron impact to the $A^3\Sigma_u^+$ metastable state. The beam from a tunable dye laser crosses the molecular beam transversely after

a transit time of several hundred microseconds, and excites the B state. The fluorescence of the B state is detected by a fast photon-counting photomultiplier tube (RCA 8852), maintained at -20°C in a cooled housing (Products for Research TE-102TS-RF). An optoacoustic modulator is used to chop the laser into pulses about 1 lifetime long, and by measuring the time at which each decay occurs the excited state lifetimes are determined.

A number of changes to the apparatus were made for the present experiment, both to increase the signal size and to improve the linearity of the timing electronics. The comparatively long lifetime of the B state also imposes severe requirements on the optical detection scheme, which has to be independent of the motion of the molecules along the beam axis. The most important modification involves cooling the beam source to 77°K . This is accomplished by flowing liquid nitrogen continuously through a copper block attached to the source slit. To reduce the heat load this source block is isolated thermally from the remainder of the electron bombarder assembly. Several advantages are accrued from the cooled beam. First, the population in the lowest rotational levels is increased by a factor of 2-3. Second, the transit time across the laser beam is doubled, making the transitions easier to saturate. Similarly the residual transverse Doppler width resulting from imperfect collimation (a collimation ratio of about 50 is used) is reduced by a factor of 2. Most important, the halving of the beam velocity reduces the average distance traveled by the molecules during a lifetime from about 3mm to about 1.5 mm and thereby makes the optical design much easier.

It was found that the operating characteristics of the electron bombarder are about the same as at room temperature, and good signals are obtained with about 4 ma of 18 eV electrons emitted from the filament of the thermionic

diode bombarder. The metastable flux appears to depend only very weakly on electron energy over the range 12-25 eV. This suggests that much of the observed A state population may arise from cascades from higher states formed by the bombarder, an interpretation also supported by the vibrational intensity distribution described below. Nitrogen is fed into the 125 μm wide source slit from a tank of ultra-pure grade nitrogen at a feed pressure of 0.25 Torr. The source region is maintained at about 2×10^{-5} Torr by an oil diffusion pump and is separated by a series of light baffles and collimators from the interaction region. The experiment takes place entirely in this collision-free low pressure region, which is maintained at about 4×10^{-7} Torr.

The laser used for these measurements is a Coherent model 699-01 ring dye laser, modified to permit single-mode operation with a 40 GHz electronic scanning range. Although some preliminary efforts were made in the red using DCM dye, all of the data reported here were taken using Rhodamine 6G dye. The dye laser output power is typically 300-600 mW, but this is attenuated by nearly a factor of 3 by the optoacoustic modulator and the various optics used for frequency measurement. The free-running laser is stable to about 10 MHz for periods of several minutes, and is easily maintained on the center of the 20 MHz wide molecular resonance lines by the slow digital locking scheme described below. A 1.5 h data-taking run could normally be accomplished without human intervention, and the long-term stability of the system is such that much longer runs are possible.

A number of different configurations of excitation and detection wavelengths were tried before a satisfactory arrangement was found. Because the A and B states have very different equilibrium separations, the Franck-Condon factors allow a given B state level to decay with significant

transition amplitude on several different bands. A table of calculated Einstein A coefficients for the first positive system appears in Lofthus and Krupenie.⁷ The most successful arrangement involves exciting the B state on one of the bluest of the strongly allowed bands, then detecting decay in a broad band to the red of the excitation frequency. For example, the 10-6 band is excited at 584 nm, and the $v'=10$ level decays primarily via the bands 10-6, 10-7 (631 nm), 10-9 (746 nm) and 10-10 (818 nm). All of the levels used for the lifetime measurements are excited on band with $\Delta v=4$, which fall in the range 585-613 nm. Sharp cutoff filters of Schott glass are placed in the optical path to eliminate scattered laser light while passing laser-induced fluorescence to the red, out to the limit of the photomultiplier response at about 850 nm. For a typical vibrational level about half of the decay light is at wavelengths that can be detected with this scheme.

The optics of the interaction region are shown in Fig. 1. A peculiarity of the B state experiment is the severe mismatch between homogeneous and inhomogeneous broadening. The lifetime of about 5 μ sec leads to a natural width of about 32 kHz, while the transverse velocity spread of the beam gives rise to a Doppler profile about 10 MHz wide. Although the laser power level needed to saturate the resonant portion of the velocity spread is very low, it is not possible to power broaden the transition sufficiently to excite the full range of velocities. This problem was solved by using a concave mirror of 15 cm radius to produce a divergent retroreflected beam with an angular spread that approximately matches that of the molecular beam. Without this mirror the signals are almost unobservably small. The fluorescent decay light is imaged onto the photomultiplier cathode by an $f/2$ optical system with provisions for inserting filters.

Even with the nitrogen cooled beam source the largest source of error in the measurements is the variation in detection efficiency with beam position. This variation was measured by translating a small light source along the beam axis and monitoring the photomultiplier counting rate. With a lens chosen to provide a circle of least confusion 1 cm in diameter on the 5 cm photocathode, variations as large as 50% were found as the light source was translated by several mm. The optical path was carefully chosen to minimize vignetting and variations in geometric collection efficiency, so the observed variation is thought to arise from spatial variations in cathode quantum efficiency. In the final experimental configuration this problem is eliminated by placing a ground glass plate between the filter and the photomultiplier. The measured detection efficiency then varies by less than 3% between the center of the aperture plate and a position 7mm away. This amounts to a change of less than 1% during the 1.5 mm drift time corresponding to one of the B state lifetimes.

The signal size is reduced by a factor of about 2 by the need to use a ground glass diffuser and an optical system with a relatively poor f number. Nevertheless, the signal to noise ratio is high, and the signals are easily located by tuning to the wavelengths calculated from the energy level tables of Dieke and Heath.⁹ The $Q_{11}(3)$ rotational branches were found to be particularly intense, and were used for all of the lifetime measurements reported in Table 1. The typical signal counting rate is 1500 counts per second above a background of 2000 counts per second, giving a signal to noise ratio of about 25:1 in 1 s. Figure 2 shows a scan over one of the stronger lines, recorded together with the fluorescence signal from an iodine cell that was used as a frequency reference. The background counts are due mostly to fluorescence from the molecular beam, although

contributions from scattered laser light, dark counts and scattered light from the bombarder filament can be observed. The beam-dependent background is almost 3 times larger at room temperature than at liquid nitrogen temperature. We believe that it arises from higher-lying metastables that cascade through the first positive system when they decay, and the threefold change in amplitude with a halving of beam velocity suggests the state has a lifetime of a few hundred μsec . A good candidate for this higher metastable species is the W state, for which lifetimes of this magnitude have been calculated in the higher vibrational levels.¹⁰

The distribution of line intensities with vibrational quantum number shows only a weak dependence, with the largest intensities coming from some of the lowest vibrational quantum numbers. Since the laser power is sufficient to saturate all of the transitions studied, this indicates that the metastable A state has large populations in the $v' = 1, 2$, and 3 states. The Franck-Condon factors indicate very little amplitude for these levels in excitation from the ground state,⁷ suggesting that they must be populated primarily by cascades from the higher states. In addition to the W state mentioned above, the electron bombarder can be expected to produce the B state and the $C^3\Pi_u$ state. Since all three of these species decay eventually to the metastable state and have larger electron impact excitation cross sections than the A state itself,¹¹ it is reasonable that a large portion of the observed A state population comes from such cascades. The contribution of many different states also explains the fact that the rate of metastable production has an extremely broad peak in electron energy.

3.4 Data Collection and Analysis

The lifetime data were acquired using an innovative arrangement in which an Intel 8088-based laboratory microcomputer entirely supplants the role of the pulse height analyzer used earlier.⁸ A schematic diagram of the timing and data acquisition electronics appears in Fig. 1. The opto-acoustic modulator (Isomet model 1250) chops the laser into pulses 5.02 μsec long, and is operated at a repetition interval of 15 μsec . The time to amplitude converter (TAC) is started whenever a decay photon is encountered and is stopped by the triggering pulse for the succeeding laser pulse. The TAC output is digitized by a Wilkinson type analog to digital converter which generates an interrupt to the microcomputer. The pulse height analysis function is performed by an assembly language routine for the microcomputer that requires about 60 μsec to calculate and increment the appropriate memory storage location. After this dead time the converter is re-enabled synchronously with the start of a laser pulse to avoid anomalies in the pileup shape that can be caused by beating between the duration of the dead time and the interval between laser pulses.

At intervals of 1 s the control program tunes the laser alternatively onto the resonance line and about 100 MHz away from it. The background data are stored in a separate array for later subtraction. Because the laser and molecular beam are both left on during background acquisition, the subtraction not only removes the constant background due to unwanted light, but eliminates any time-dependent effects coming from the laser pulse and the weak fluorescence it induces in the Schott glass filter. A small dither is applied to the laser frequency by setting it to a slightly different frequency each time signal acquisition begins. By examining the signal sizes and filtering them using a digital control algorithm,¹² the

computer is able to lock the laser frequency to the molecular resonance line. All the while, a display of the signal is provided on the computer console. After a data run has been completed the signal and background arrays are first corrected for pileup on a channel-by-channel basis. This is a small correction, typically about 3% for the channel experiencing the maximum pileup. The background array is then normalized to reflect the difference in live counting time between the signal and background, and is subtracted from the signal array.

The decay curves were badly distorted by the effects of Zeeman quantum beats when taken in the earth's magnetic field. The 20 gauss field of a small permanent magnet is used to make the beats ignorably weak and very fast compared with a lifetime.

After performing these corrections a least-squares fit to an exponential is performed. The background subtraction obviates the need to include a background term as a fitting parameter, although all runs are also fitted with this term included to ascertain that the background is consistent with zero. The lifetimes show no significant variation when the starting channel is varied. In Figure 3 the decay curve of the $J=4$ level of $v=6$ is shown together with the fit. The peculiar shape of the laser pulse as observed in fluorescence light is easily explained. Initially the signal rises steeply as the beam saturates the transition in any molecules that are initially present; the signal then rises linearly as new molecules drift into the laser path.

3.5 Error Analysis

The laser-molecular beam method avoids many of the potential sources for systematic error that afflict lifetime measurements. Collisional and

light trapping effects are negligible because of the very low pressures and counting rates in the molecular beam apparatus, and the effects of Zeeman quantum beats are easily eliminated by using a small magnet. This section discusses the remaining sources of possible shifts in the apparent lifetimes.

As a check on the quality of the data several runs were repeated under varying conditions of laser power, counting rates and pulse repetition time. The results of the repeated runs are basically consistent with the statistical errors, although there is a suggestion that the statistical errors, which are typically about 1-2%, are about 20% too small. Such a small increase in the error budget may arise from the remaining variation in detection efficiency with beam position, since the point at which the laser and molecular beams intersect can vary by 1-2 mm between runs. Much more important than these small fluctuations is the average size of the shift in lifetime these variations could cause. To conservatively take into account this potential shift a 3% systematic error was added in quadrature with each lifetime determination. This is about 3 times the size of the error estimated by using the measured variations in detection efficiency. In nearly all cases, this 3% error totally dominates the overall error.

A potentially serious error is the possibility of confusing the desired decay channel with cascades through the path $B \rightarrow W \rightarrow B \rightarrow A$. The long estimated lifetime of the W state¹⁰ makes it very unlikely that this pathway could distort the apparent lifetime by much more than 1%. Nevertheless, some simple experiments were performed to make sure that such distortion is not occurring. The first such experiment consisted of examining the decays of the $v=6$ and $v=7$ levels through interference filters that selected the 6-3 and 7-4 decay bands. Unfortunately, the accuracy of lifetime measure-

ments made under these conditions is limited by a relatively large shift caused by angle tuning of the interference filter. As the molecules travel down the beam line the mean angle through the filter increases, and an increasing amount of the decay light is shifted outside of the filter pass-band. Apparent lifetime shifts in the range of 0-8% are observed for various tipping angles of the filters. These shifts agree well with estimates based on the decrease in total signal size as the filters are tipped, but the estimates are not accurate to much better than 5%. Thus it can be concluded only that there is no evidence for effects on the $v=6$ and 7 lifetimes at the 5% level.

A second search for the effects of intra-system cascading was made by looking for decay light through a filter that selected the 2-0 band of the first positive system. Published A coefficients for the $B \rightarrow W$ and $W \rightarrow B$ decays¹⁰ suggest that most of the cascading would take place through B state levels with $v=0, 1$, and 2. The 2-0 band is the only one arising from these levels that can be observed with the 8852 photomultiplier. No evidence was found for laser-induced fluorescence on this band when the laser was tuned to the $v=6, 7$, and 10 levels, indicating that the cascade light on this band is present at a level no greater than 5% of the normal signal size. In addition, any distortion of the B state lifetimes is a second order effect, reduced both by the relative weakness of the cascade light and by the fact that fits to a single exponential are shifted only slightly by the presence of a component with a longer lifetime. The results of these two experiments indicate that intra-system cascading has no significant effect on the lifetime measurements, although a contribution of up to 5% cannot be ruled out.

3.6 Discussion

The lifetimes given in Table I include the 3% systematic error described in the previous section. An examination of the table shows that the results of the present measurement are in fairly close agreement with those of Jeunehomme,¹ although the Jeunehomme results appear to be systematically too large by about 5-10%. The agreement with Hollstein, et al.³ is also good, although their results again indicate slightly longer lifetimes. The same cannot be said of the other existing measurements, which in general show very short lifetimes and weak or erratic vibrational variations. Since these measurements were made using methods similar to those of Jeunehomme,¹ it is not entirely clear why they disagree. Apparently the spectrum of higher excited states that can contribute cascade radiation after an unselective excitation pulse is somewhat richer than had been suspected.

Since the resolution of the laser system is easily sufficient to resolve the rotational structure, a brief search was made for rotational dependence of the lifetimes. Measurements of the $J' = 2, 3, 4, 5, 7$ and 8 levels of the $v=6$ vibrational level are summarized in Table II; they show no significant variation. This is in accord with the observation of Dieke and Heath⁹ that the B state is nearly free from perturbations with neighboring states.

The only theoretical calculation of the B state lifetimes is in an article by Breene,¹³ and is apparently not of sufficient accuracy to constitute a real test of the experimental values. Transition moments for the first positive system have been calculated both from the results of Jeunehomme¹ and from an approach by Shemansky and Broadfoot⁵ that combines relative intensity measurements with a single lifetime measurement. The ac-

curate lifetimes given here largely confirm the accuracy of these transition moments, since the lifetime measurements are in agreement with Jeunehomme's measurements to within 10%. The much weaker variation with the vibrational level indicated by most of the recent lifetime measurements can be ruled out.

4.0 Studies of Higher Rydberg States

4.1 Motivation

To understand the spectrum of radiation emitted through excitation of the atmosphere by particle bombardment from either extra terrestrial or terrestrial sources, it is necessary to have a complete understanding of the mechanisms for excitation and decay of molecular nitrogen which is the dominant component of the atmosphere. The nitrogen molecule is quite unique in that it has a large number of rather high lying metastable states. Figure 4 shows in the form of an energy level diagram, the relative location of the many metastable states. These states serve as bottlenecks for the radiative decay of molecular nitrogen and as access points for excitation into high lying Rydberg states which are potential sources of infrared radiation. The high energy of the metastable states and the Rydberg states makes them suitable doorways for exothermic chemical reactions. To understand the molecular dynamics of electron-beam excited gas samples, it is essential to understand the role of the Rydberg states and the metastable states. The relative probability for the Rydberg states to predissociate into excited nitrogen atoms and to decay radiatively is an essential ingredient for understanding the excitation and decay of atmospheric disturbances.

Despite a great deal of work by many investigators over the last century, our understanding of molecular nitrogen is still incomplete.⁷

There is, in particular, little knowledge of the Rydberg states and no knowledge of the role of the Rydberg states in the excitation and decay of molecular nitrogen. There is very little information concerning the relative probability of the Rydberg states to decay through predissociation and radiative decay to lower energy states. It was the purpose of this task to explore techniques through which one can study the high lying Rydberg states of N_2 .

4.2 Method

The same apparatus used to measure the lifetimes for the $B^3\Pi_g$ state of N_2 was used to look for excitation of the Rydberg states in N_2 . A crossed electron beam was used to excite N_2 molecules from the ground state up into the metastable states and in particular the $a''^1\Sigma_g^+$ metastable state. The output of the Coherent 599 dye laser was then used to excite the metastable molecules up into the $c_4(0)^1\Pi_u$ or $c_5'(0)^1\Sigma_u^+$ Rydberg levels and the excitation was detected through observation of the fluorescent radiation. These levels have been observed by Suzuki and Kakimoto¹⁴ and by Mizazki, et al.¹⁵ by using opto-galvanic spectroscopy. The $c_4(0)^1\Pi_u$ state has been observed in uv emission through the observation of an N_2 discharge by a uv spectrometer.^{7,16-18}

The experiment is made difficult by the small cross section for electron beam excitation of the $a''(0)^1\Sigma_g^+$ metastable state^{11,19,20} and by the unknown lifetime for this metastable state.⁷ The lifetime has never been measured and experiments using shock tube excitation to observe this level suggest that it could be as short as 10 μ sec.

4.3 Results

For the first attempt to detect the excitation of the $c_4(0) \ ^1\Pi_u$ and $c'_5(0) \ ^1\Sigma_g^+$ Rydberg states we used the same set up that we employed for the measurement of the lifetimes of the $B^3\Pi_g$ state. The red sensitive photomultiplier tube was used to detect the fluorescent radiation. We first tried this experiment with a room temperature N_2 beam and observed what appeared to be small fluorescent signals. These signals disappeared when we cooled the beam. This suggested that the lifetime of the $a'' \ ^1\Sigma_g^+$ state was short and that when the beam was cooled the atoms in this state did not live long enough to reach the region where the dye laser beam crossed the molecular beam. The background count rate in the photomultiplier was high due to general radiation emitted by the excited N_2 atoms. This limited the sensitivity of the experiment.

For the second series of experiments we replaced the cooled photomultiplier tube by a channeltron detector which was sensitive to uv radiation such as would be emitted by the Rydberg states through direct decay to the ground state of N_2 . In these experiments we observed some signals which were suggestive of fluorescent signals but we were not able to increase the signal to noise sufficiently to make them believable. The experiments were quite encouraging in that the background with the channeltron was low so that we were sensitive to smaller signals than with the red sensitive photomultiplier tube.

For the third series of experiments we reconfigured the apparatus so as to decrease as much as was mechanically possible the distance from the source of metastable molecules to the point where the laser beam intersected the molecular beam. We then used the channeltron detector to search for excitation of the $c_4(0) \ \Pi_u$ and $c'_5(0) \ ^1\Sigma_u^+$ metastable states.

We had very good runs, but were not able to detect any fluorescent radiation from the Rydberg states. This could be attributed either to a small cross section for electron beam excitation of the $a'' \ ^1\Sigma_g^+$ metastable state or the short lifetime for this metastable state. The measured excitation cross section^{11,19,20} for the $a'' \ ^1\Sigma_g^+$ state suggests that the excitation should not be a problem so the failure must be attributed to the short lifetime of the metastable state. The present design of the beam apparatus is such that if the lifetime of the metastable state was less than 100 μ s, a sufficient number of metastable molecules would not reach the detector to produce an observable signal. We thus attribute the failure to see a signal to the short lifetime.

Since it was impossible to decrease further the distance between the metastable source and the detection region without a major rebuilding of the apparatus, we started an investigation of other methods for obtaining a source of N_2 molecules in the $a'' \ ^1\Sigma_g^+$ metastable state. It is particularly attractive to use a discharge source since we could easily decrease the distance between the discharge source and the detection region by inputting the beam from the opposite end of the beam apparatus. We also have a discharge source which was built for an earlier experiment.

As a first step in this investigation we explored the use of optogalvanic spectroscopy as a means for determining the optimum discharge conditions for production of the $a'' \ ^1\Sigma_g^+$ metastable state. This will also enable us to repeat the work of Suzuki and Kakimoto¹⁴ and Miyazaki, et al.¹⁵ and possibly extend these measurements to other states. These experiments were in process at the time the contract period ended. We had learned to successfully detect for optogalvanic signals from neon and were preparing to look at the signals from N_2 .

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6.0 Tables

6.1 Table 1. A summary of the measured values for the lifetimes of the vibrational levels of the $B^3\Pi_g$ state of molecular nitrogen. The methods and estimated errors are described at the bottom of the table.

v	Ref. 1	Ref. 2	Ref. 3	Ref. 4	Ref. 5	Ref. 6	This Work
0	8.0	-	-	-	-	4.9	-
1	7.5	-	-	-	-	4.5	-
2	7.0	3.5	7.5 ± 0.20	-	-	4.6	-
3	6.8	3.2	6.6 ± 0.30	3.3	6.5	4.7	-
4	6.5	2.6	-	4.0	-	5.5	-
5	6.2	2.4	6.1 ± 0.20	3.5	-	5.1	5.87 ± 0.21
6	6.0	2.3	-	4.0	-	5.5	5.34 ± 0.17
7	5.3	2.7	-	4.3	-	5.0	5.05 ± 0.16
8	5.1	2.2	-	4.0	-	4.5	4.72 ± 0.15
9	4.8	-	4.87 ± 0.25	-	-	4.0	4.41 ± 0.15
10	4.4	-	-	-	-	5.1	4.33 ± 0.17
11	-	-	-	-	-	4.9	4.19 ± 0.17
12	-	-	4.14 ± 0.15	-	-	5.0	4.11 ± 0.21

1. Pulsed rf discharge, 10-20%.
2. Pulsed discharge, no errors quoted.
3. Beam time of flight measurement, errors shown in table.
4. Short-pulsed electron bombardment, no errors quoted.
5. Pulsed electron gun excitation, no errors quoted.
6. Pulsed electron beam excitation, 20%.

6.2 Table II. Lifetimes of some rotational levels of the $\nu=6$ state.

J	τ (μsec)
2	5.54 ± 0.24
3	5.60 ± 0.28
4	5.30 ± 0.17
5	5.38 ± 0.18
7	5.35 ± 0.26
8	5.41 ± 0.19

7.0 Figure Captions

1. Lifetime measurement apparatus, showing detection optics and electronics for data acquisition. Line marked ' Δf ' controls dye laser frequency.
2. Laser scan over the $O_{11}(3)$ branch of the 6-2 band. Top trace shows absorption spectrum of molecular iodine. The two indicated lines are separated by 0.27 cm^{-1} .
3. (a) Decay curve of the $J=4$ level of $v=6$, excited on the $O_{11}(3)$ branch, after background subtraction. Solid line shows fit to a single exponential. (b) Log plot of the same decay curve, showing portion where fit was performed.
4. An energy level diagram showing the metastable levels of N_2 .

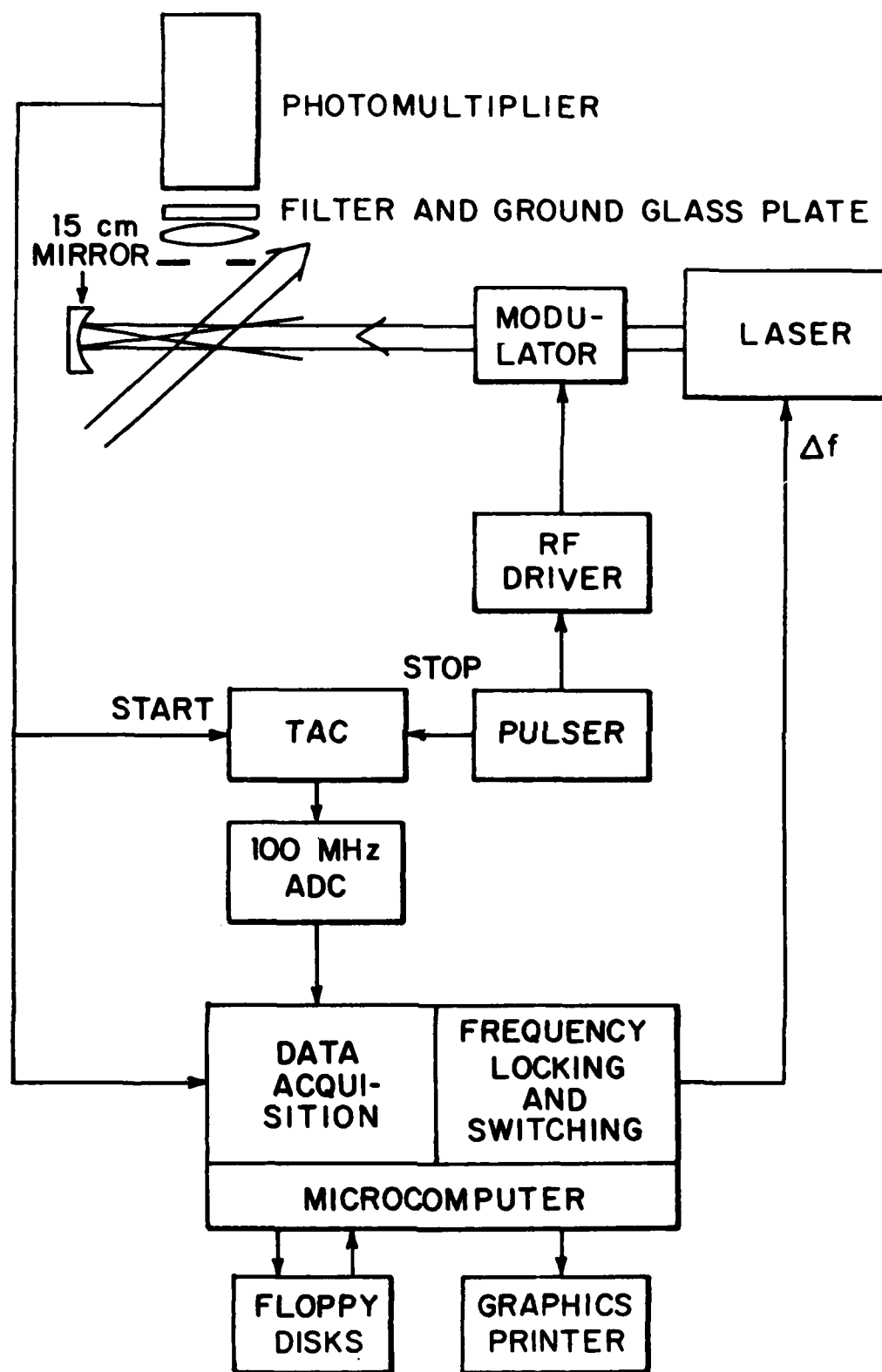


Figure 1

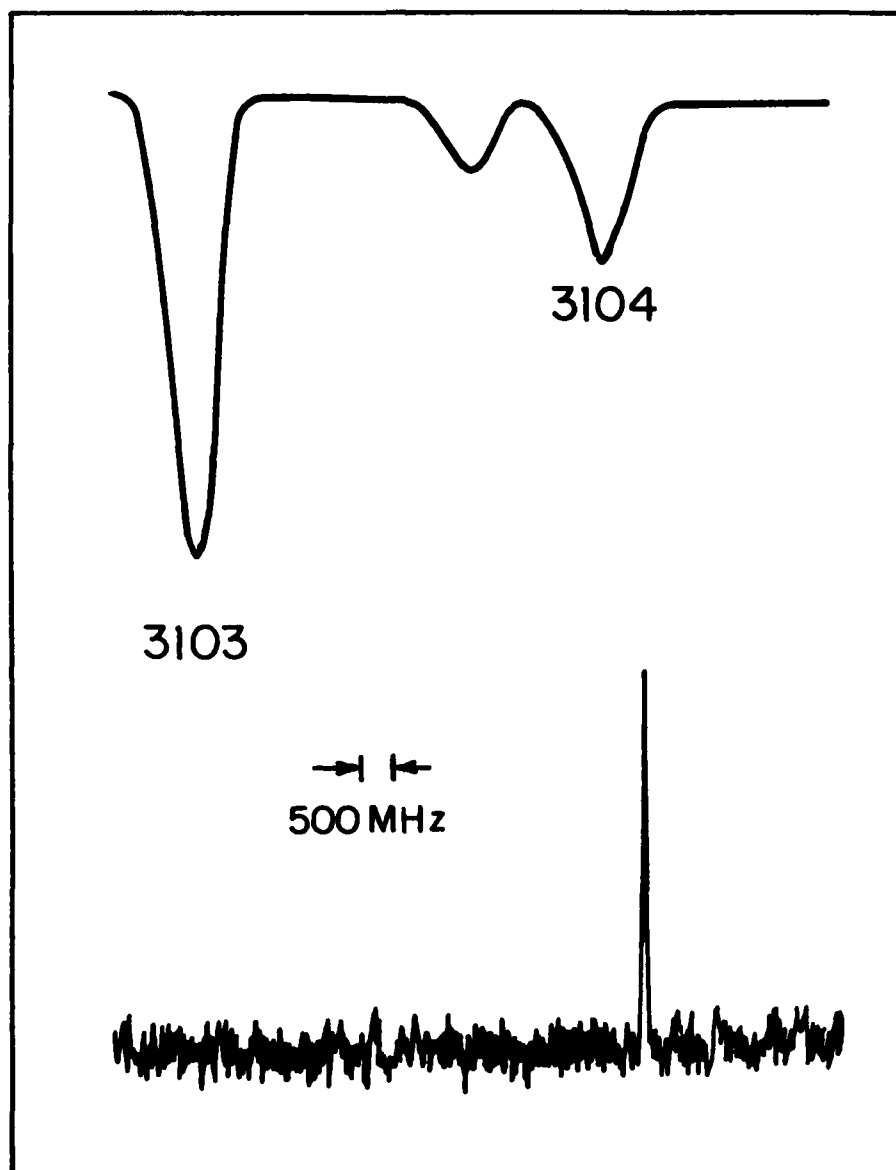


Figure 2

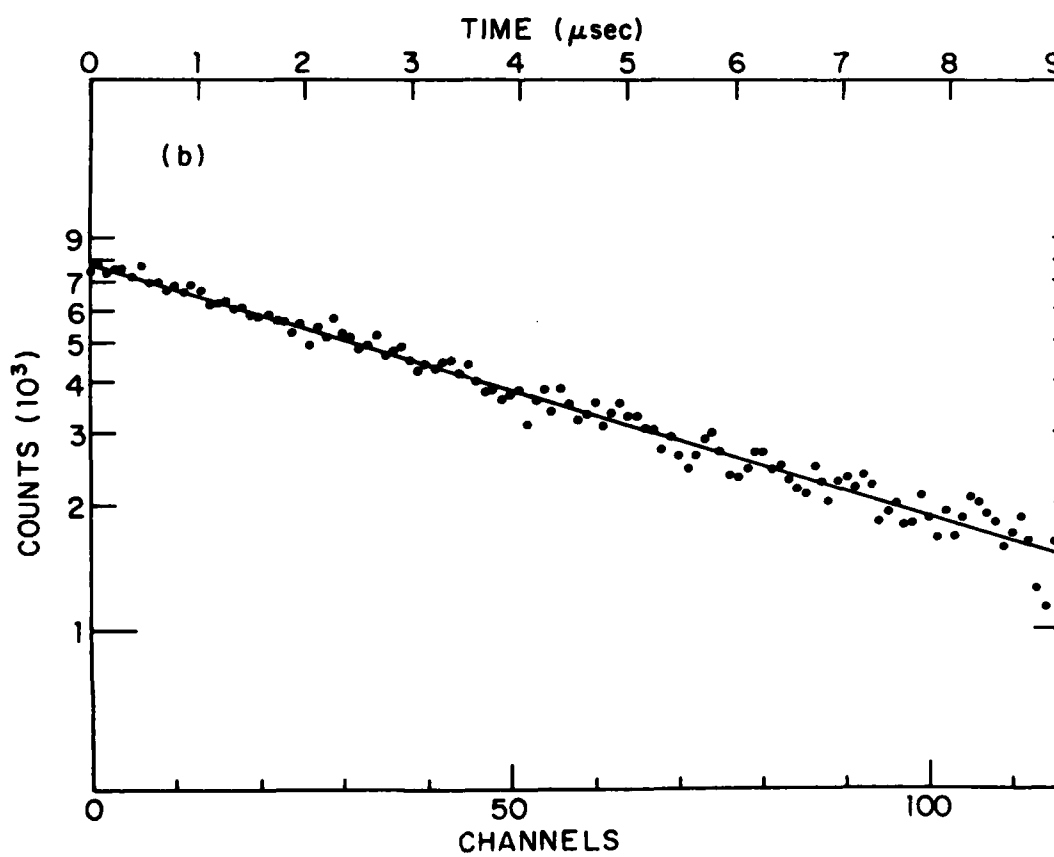
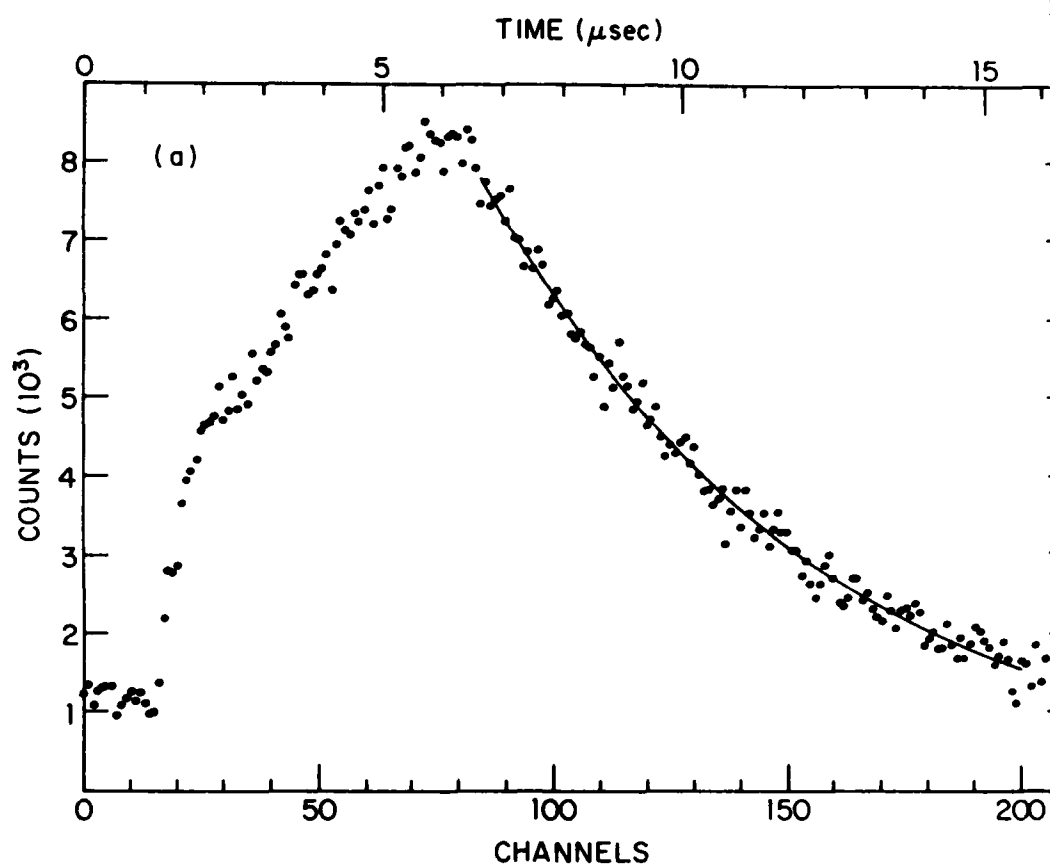


Figure 3

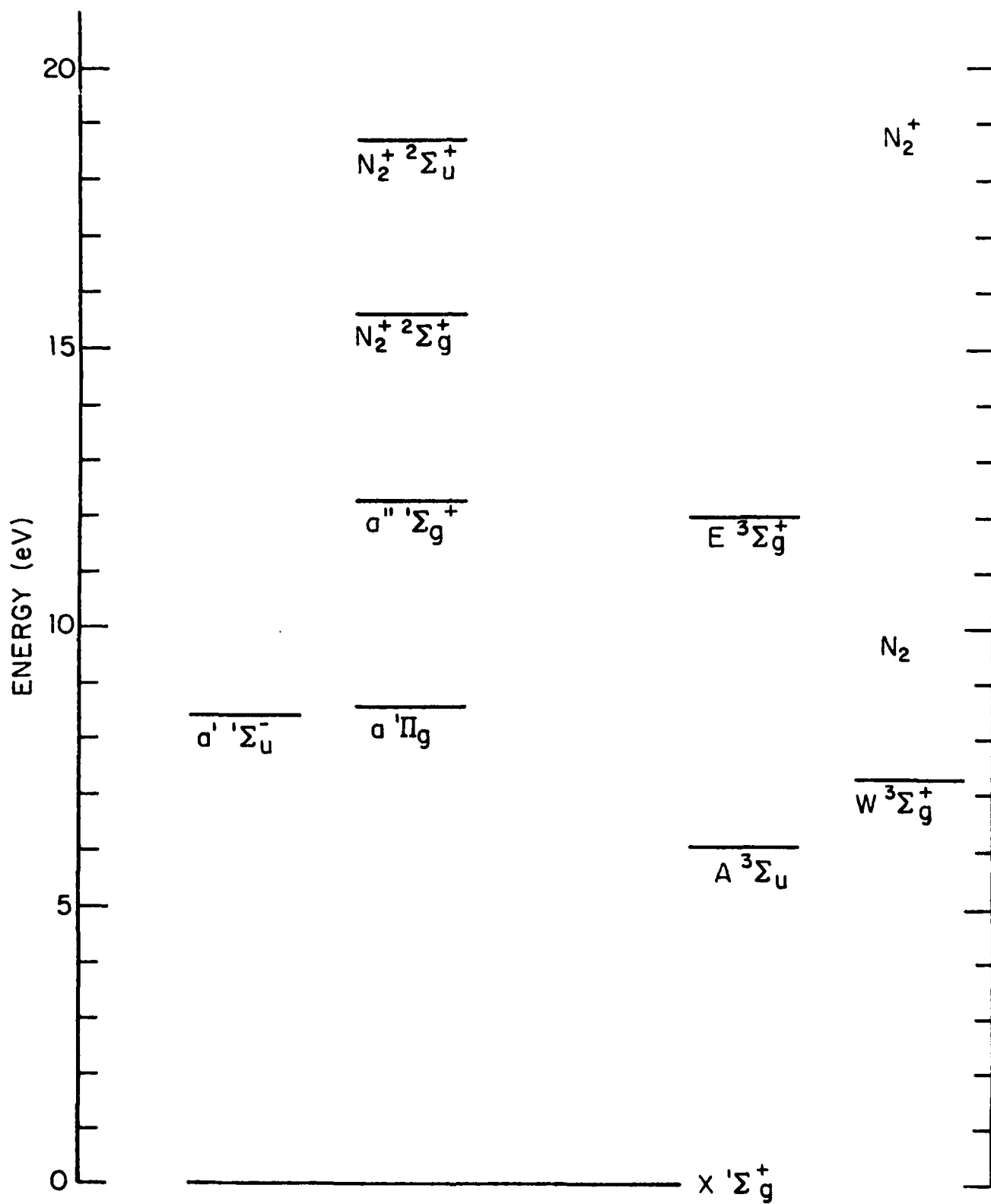


Figure 4

8.0 Personnel

During the course of the project, the following individuals participated:

F. M. Pipkin	Principal Investigator
E. E. Eyler	Research Associate
J. Schussler	Graduate Student
A. Quillen	Undergraduate

9.0 Publication

The results of the measurements on the lifetimes of the levels of the $B^3\Pi_g$ state of N_2 have been published in the Journal of Chemical Physics. The reference is:

E. E. Eyler and F. M. Pipkin, J. Chem. Phys. 79, 3654 (1983).

10.0 Appendix

A copy of the paper reporting the measurement of the lifetimes of the levels of the $B^3\Pi_g$ state of N_2 follows.

Lifetime measurements of the $B^3\Pi_g$ state of N_2 using laser excitation

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A chopped cw dye laser has been used to excite selected levels of the $B^3\Pi_g$ state of N_2 in a molecular beam of $A^1\Sigma_u^+$ state metastables. Laser-induced fluorescence was observed from the vibrational levels $v = 5$ through $v = 12$, and a photomultiplier was used in conjunction with a microcomputer system to perform time-resolved detection of the decay light. The lifetimes have been measured to an accuracy of about 3%. They show a smooth decline from 5.87 μ s for $v = 5$ to 4.11 μ s for $v = 12$. No dependence on rotational level was observed, and no contributions to the B state decay were found from intrasystem cascading of the form $B \rightarrow W^3\Delta_u \rightarrow B \rightarrow A^1\Sigma_u^+$.

INTRODUCTION

Since the $B-A$ first positive system of nitrogen is its most prominent visible band system under most discharge conditions, the lifetimes of the $B^3\Pi_g$ state are of particular importance. In addition, the B state is the lower state of the UV nitrogen laser. It is therefore not surprising that the B state lifetimes have been measured several times.¹⁻⁶ The first six columns of Table I summarize the existing measurements, which have estimated errors of about 10%–20% except for the measurement by Hollstein *et al.*³ An examination of the table shows that these measurements are in severe disarray, with disagreements by more than a factor of 2 in some cases. The recent results from Refs. 4 and 6 indicate lifetimes that are essentially independent of the vibrational quantum number, in strong contradiction with all of the earlier results. All of these measurements were performed by fitting the multiexponential decay following pulsed excitation of many electronic states, with the exception of the time-of-flight technique of Hollstein. They were all to some degree subject to cascade contributions from higher-lying species that were excited at the same time as the B state. Most of the experiments also involved an extrapolation to zero pressure. A recent review article by Lofthus and Krupenie⁷ suggests that only a better means of excitation can resolve the discrepancies between these various measurements.

We have accomplished this by using a dye laser to excite levels of the B state with complete selectivity, so that only a single rotational and vibrational level can contribute to the observed decay. A photomultiplier was used in conjunction with a microcomputer system to perform time-resolved detection of the decay light. This technique is intrinsically free from most sources of potential systematic error. Experiments were performed to search for the effects of intrasystem cascading through the decay channel $B_{(v,10)} \rightarrow W^3\Delta_u \rightarrow B_{(v,w)}$, and no effects on the measured lifetimes were found. This was not possible in earlier work because it is only by using both selective excitation and selective detection that the desired decay can be separated cleanly from intrasystem cascades. The results of the present

measurements are shown in the final column of Table I. The lifetimes show a smooth monotonic decrease with vibrational quantum number, and agree fairly well in both magnitude and vibrational dependence with the results of Jeunehomme¹ and Hollstein *et al.*²

EXPERIMENTAL

Excitation and detection of the $B^3\Pi_g$ state

The apparatus used for this work is similar to an arrangement used previously to measure the lifetimes of some $n = 3$ states in H_2 .⁸ The molecular potentials of the states involved are shown in Fig. 1. Briefly, a molecular beam is formed by effusion through a narrow slit, and a fraction of the beam is excited by electron impact to the metastable state. The beam from a tunable dye laser crosses the molecular beam transversely after a transit time of several hundred microseconds, and excites the B state. The fluorescence of

TABLE I. Summary of the measured values for the lifetimes of the vibrational levels of the $B^3\Pi_g$ state of molecular nitrogen. The methods and estimated errors are described at the bottom of the table.

v	a	b	c	d	e	f	This work
0	8.0	4.9	...
1	7.5	4.5	...
2	7.0	3.5	7.5 \pm 0.20	4.6	...
3	6.8	3.2	6.6 \pm 0.30	3.3	6.5	4.7	...
4	6.5	2.6	...	4.0	...	5.5	...
5	6.2	2.4	6.1 \pm 0.20	3.5	...	5.1	5.87 \pm 0.21
6	6.0	2.3	...	4.0	...	5.5	5.34 \pm 0.17
7	5.3	2.7	...	4.3	...	5.0	5.05 \pm 0.16
8	5.1	2.2	...	4.0	...	4.5	4.72 \pm 0.15
9	4.8	...	4.87 \pm 0.25	4.0	4.41 \pm 0.15
10	4.4	5.1	4.33 \pm 0.17
11	4.9	4.19 \pm 0.17
12	4.14 \pm 0.15	5.0	4.11 \pm 0.21

^aPulsed rf discharge, 10%–20%, Ref. 1.

^bPulsed discharge, no errors quoted, Ref. 2.

^cBeam time of flight measurement, errors shown in the table, Ref. 3.

^dShort-pulse electron bombardment, no errors quoted, Ref. 4.

^ePulsed electron gun excitation, no errors quoted, Ref. 5.

^fPulsed electron beam excitation, 20%, Ref. 6.

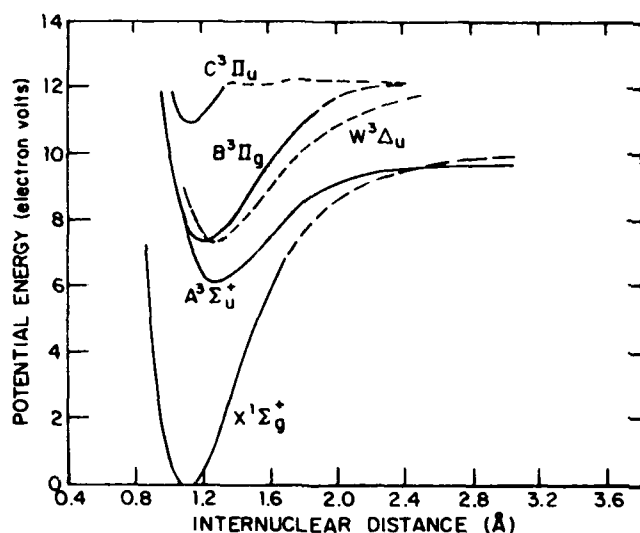


FIG. 1. Potential curves for the N_2 states involved in the experiment. The W state is both a source of metastable population and a possible intermediate in an alternative decay path $B \rightarrow W \rightarrow B \rightarrow A$. Potentials are taken from Ref. 7.

the B state is detected by a fast photon-counting photomultiplier tube (RCA 8852), maintained at -20°C in a cooled housing (Products for Research TE-102TS-RF). An acousto-optic modulator is used to chop the laser into pulses about $\frac{1}{2}$ lifetime long, and by measuring the time at which each decay occurs the excited state lifetimes are determined directly.

A number of changes to the apparatus were made for the present experiment, both to increase the signal size and to improve the linearity of the timing electronics. The comparatively long lifetime of the B state also imposes severe requirements on the optical detection scheme, which has to be independent of the motion of the molecules along the beam axis. The most important modification involves cooling the beam source to 77 K. This is accomplished by flowing liquid nitrogen continuously through a copper block attached to the source slit. To reduce the heat load this source block is isolated thermally from the remainder of the electron bombarder assembly. Several advantages are accrued from the cooled beam. First, the population in the lowest rotational levels is increased by a factor of 2–3. Second, the transit time across the laser beam is doubled, making the transitions easier to saturate. Similarly the residual transverse Doppler width resulting from imperfect collimation (a collimation ratio of about 50 is used) is reduced by a factor of 2. Most important, the halving of beam velocity reduces the average distance traveled by the molecules during a lifetime from about 3 to about 1.5 mm and thereby makes the optical design much easier.

It was found that the operating characteristics of the electron bombarder are about the same as at room temperature, and good signals are obtained with about 4 ma of 18 eV electrons emitted from the filament of the thermionic diode bombarder. The metastable flux appears to depend only very weakly on electron energy

over the range 12–25 eV. This suggests that much of the observed A state population may arise from cascades from higher states formed by the bombarder, an interpretation also supported by the vibrational intensity distribution described below. Nitrogen is fed into the 125 μm wide source slit from a tank of ultrapure grade nitrogen at a feed pressure of 0.25 Torr. The source region is maintained at about 2×10^{-5} Torr by an oil diffusion pump and is separated by a series of light baffles and collimators from the interaction region. The experiment takes place entirely in this collision-free low pressure region, which is maintained at about 4×10^{-7} Torr.

The laser used for these measurements is a Coherent model 699-01 ring dye laser, modified to permit single-mode operation with a 40 GHz electronic scanning range. Although some preliminary efforts were made in the red using DCM dye, all of the data reported here were taken using Rhodamine 6G dye. The dye laser output power is typically 300–600 mW, but this is attenuated by nearly a factor of 3 by the optoacoustic modulator and the various optics used for frequency measurement. The ring laser is a major improvement over the standing-wave dye laser used for our earlier work primarily because of its stability. The free-running laser is stable to about 10 MHz for periods of several minutes, and is easily maintained on the center of the 20 MHz wide molecular resonance lines by the slow digital locking scheme described below. A 1.5 h data-taking run could normally be accomplished without human intervention, and the long-term stability of the system is such that much longer runs are possible.

A number of different configurations of excitation and detection wavelengths were tried before a satisfactory arrangement was found. Because the A and B states have very different equilibrium separations, the Franck-Condon factors allow a given B state level to decay with significant transition amplitude on several different bands. A table of calculated Einstein A coefficients for the first positive system appears in Lofthus and Krupenie.⁷ The most successful arrangement involves exciting the B state on one of the bluest of the strongly allowed bands, then detecting decay in a broad band to the red of the excitation frequency. For example, the 10–6 band is excited at 584 nm, and the $v' = 10$ level decays primarily via the bands 10–6, 10–7 (631 nm), 10–9 (746 nm), and 10–10 (818 nm). All of the levels used for the lifetime measurements are excited on bands with $\Delta v = 4$, which fall in the range 585–613 nm. Sharp cutoff filters of Schott glass are placed in the optical path to eliminate scattered laser light while passing laser-induced fluorescence to the red, out to the limit of the photomultiplier response at about 850 nm. For a typical vibrational level about half of the decay light is at wavelengths that can be detected with this scheme.

The optics of the interaction region are shown in Fig. 2. A peculiarity of the B state experiment is the severe mismatch between homogeneous and inhomogeneous broadening. The lifetime of about 5 μs leads to a natural width of about 32 kHz, while the transverse velocity

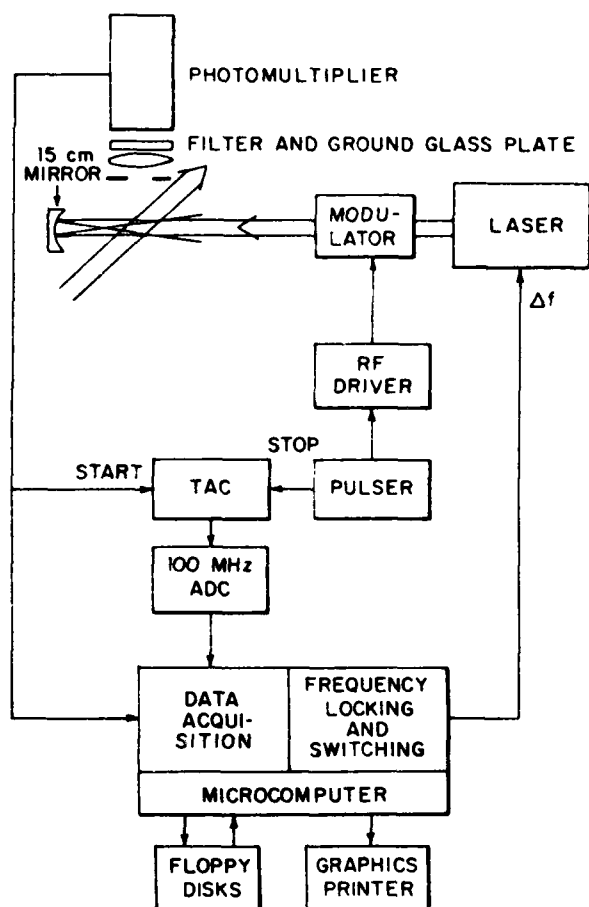


FIG. 2. Lifetime measurement apparatus, showing detection optics and electronics for data acquisition. Line marked Δf controls dye laser frequency.

spread of the beam gives rise to a Doppler profile about 10 MHz wide. Although the laser power level needed to saturate the resonant portion of the velocity spread is very low, it is not possible to power broaden the transition sufficiently to excite the full range of velocities. This problem was solved by using a concave mirror of 15 cm radius to produce a divergent retroreflected beam with an angular spread that approximately matches that of the molecular beam. Without this mirror the signals are almost unobservably small. The fluorescent decay light is imaged onto the photomultiplier cathode by an $f/2$ optical system with provisions for inserting filters.

Even with the nitrogen cooled beam source the largest source of error in the measurements is the variation in detection efficiency with beam position. This variation was measured by translating a small light source along the beam axis and monitoring the photomultiplier counting rate. With a lens chosen to provide a circle of least confusion 1 cm in diameter on the 5 cm photocathode, variations as large as 50% were found as the light source was translated by several mm. The optical path was carefully chosen to minimize vignetting and variations in geometric collection efficiency, so the observed variation is thought to arise from spatial fluctuations in cathode quantum efficiency. In the final experi-

mental configuration this problem is eliminated by placing a ground glass plate between the filter and the photomultiplier. The measured detection efficiency then varies by less than 3% between the center of the aperture plate and a position 7 mm away. This amounts to a change of less than 1% during the 1.5 mm drift time corresponding to one of the B state lifetimes.

The signal size is reduced by a factor of about 2 by the need to use a ground glass diffuser and an optical system with a relatively poor f number. Nevertheless the signal-to-noise ratio is high, and the signals are easily located by tuning to the wavelengths calculated from the energy level tables of Dicke and Heath.⁹ The $Q_{11}(3)$ rotational branches were found to be particularly intense, and were used for all of the lifetime measurements reported in Table I. The typical signal counting rate is 1500 counts per second above a background of 2000 counts per second, giving a signal to noise ratio of about 25:1 in 1 s. Figure 3 shows a scan over one of the stronger lines, recorded together with the fluorescence signal from an iodine cell that was used as a frequency reference. The background counts are due mostly to fluorescence from the molecular beam, although contributions from scattered laser light, dark counts, and scattered light from the bombarder filament can all be observed. The beam-dependent background is almost three times larger at room temperature than at liquid nitrogen temperature. We believe that it arises from higher-lying metastables that cascade through the first positive system when they decay, and the threefold change in amplitude with a halving of beam velocity suggests the state has a lifetime of a few hundred μ s. A good candidate for this higher metastable species is the W state, for which lifetimes of this magnitude have been calculated in the higher vibrational levels.¹⁰

The distribution of line intensities with vibrational

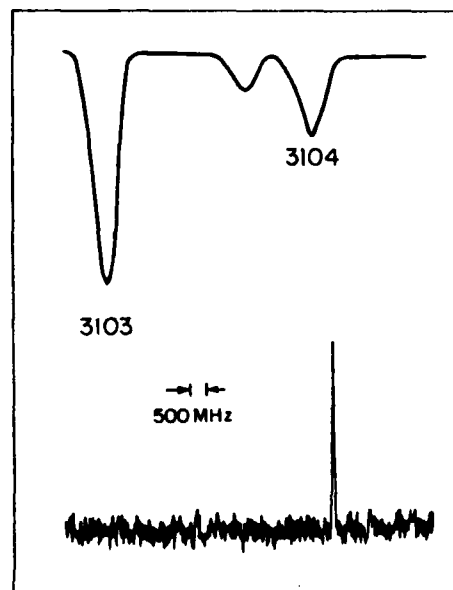


FIG. 3. Laser scan over the $Q_{11}(3)$ branch of the 6-2 band. Top trace shows absorption spectrum of molecular iodine. The two indicated lines are separated by 0.27 cm^{-1} .

quantum number shows only a weak dependence, with the largest intensities coming from some of the lowest vibrational quantum numbers. Since the laser power is sufficient to saturate all of the transitions studied, this indicates that the metastable A state has large populations in the $n'' = 1, 2$, and 3 states. The Franck-Condon factors indicate very little amplitude for these levels in excitation from the ground state,⁷ indicating that they must be populated primarily by cascades from the higher states. In addition to the W state mentioned above, the electron bombardment can be expected to produce the B state and the $C^3\Pi_u$ state. Since all three of these species decay eventually to the metastable state and have larger electron impact excitation cross sections than the A state itself,¹¹ it is reasonable that a large portion of the observed A state population comes from such cascades. The contribution of many different states also explains the fact that the rate of metastable production has an extremely broad peak in electron energy.

Data acquisition and analysis

The lifetime data were acquired using an innovative arrangement in which an Intel 8088-based laboratory microcomputer entirely supplants the role of the pulse height analyzer used earlier.⁸ A schematic diagram of the timing and data acquisition electronics appears in Fig. 2. The optoacoustic modulator (Isomet model 1250) chops the laser into pulses 5.02 μ s long, and is operated at a repetition interval of 15 μ s. The time to amplitude converter (TAC) is started whenever a decay photon is encountered and is stopped by the triggering pulse for the succeeding laser pulse. The TAC output is digitized by a Wilkinson type analog to digital converter which generates an interrupt to the microcomputer. The pulse height analysis function is performed by an assembly language routine for the microcomputer that requires about 60 μ s to calculate and increment the appropriate memory storage location. After this dead time the converter is reenabled synchronously with the start of a laser pulse, to avoid anomalies in the pileup shape that can be caused by beating between the duration of the dead time and the interval between laser pulses.

At intervals of 1 s the control program tunes the laser alternately onto the resonance line and about 100 MHz away from it. The background data are stored in a separate array for later subtraction. Because the laser and molecular beam are both left on during background acquisition, the subtraction not only removes the constant background due to unwanted light, but eliminates any time-dependent effects coming from the laser pulse and the weak fluorescence it induces in the Schott glass filter. A small dither is applied to the laser frequency by setting it to a slightly different frequency each time signal acquisition begins. By examining the signal sizes and filtering them using a digital control algorithm,¹² the computer is able to lock the laser frequency to the molecular resonance line. All the while, a display of the signal is provided on the computer console. After a data run has been completed the signal and background arrays are first corrected for pileup on a channel-by-channel basis. This is a small correction, typically

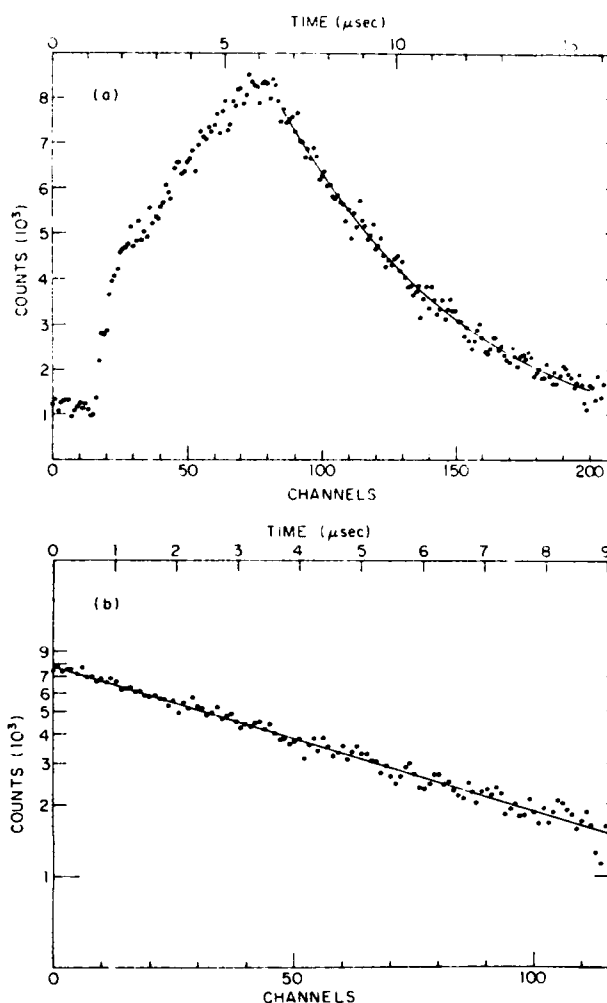


FIG. 4. (a) Decay curve of the $J = 4$ level of $v = 6$, excited on the $Q_{11}(3)$ branch, after background subtraction. Solid line shows fit to a single exponential. (b) Log plot of the same decay curve, showing portion where fit was performed.

about 3% for the channel experiencing the maximum pileup. The background array is then normalized to reflect the difference in live counting time between the signal and background, and is subtracted from the signal array.

The decay curves were badly distorted by the effects of Zeeman quantum beats when taken in the earth's magnetic field. The 20 G field of a small permanent magnet is used to make the beats ignorably weak and very fast compared with a lifetime.

After performing these corrections a least-squares fit to an exponential is performed. The background subtraction obviates the need to include a background term as a fitting parameter, although all runs are also fitted with this term included to ascertain that the background is consistent with zero. The lifetimes show no significant variation when the starting channel is varied. In Fig. 4 the decay curve of the $J = 4$ level of $v = 6$ is shown together with the fit. The peculiar shape of the laser pulse as observed in fluorescence light is easily ex-

plained. Initially the signal rises steeply as the beam saturates the transition in any molecules that are initially present; the signal then rises linearly as new molecules drift into the laser path.

Error analysis

The laser-molecular beam method avoids many of the potential sources for systematic error that afflict lifetime measurements. Collisional and light trapping effects are negligible because of the very low pressures and counting rates in the molecular beam apparatus, and the effects of Zeeman quantum beats are easily eliminated by using a small magnet. This section discusses the remaining sources of possible shifts in the apparent lifetimes.

As a check on the quality of the data several runs were repeated under varying conditions of laser power, counting rates, and pulse repetition time. The results of the repeated runs are basically consistent with the statistical errors, although there is a suggestion that the statistical errors, which are typically about 1%–2%, are about 20% too small. Such a small increase in the error budget may arise from the remaining variation in detection efficiency with beam position, since the point at which the laser and molecular beams intersect can vary by 1–2 mm between runs. Much more important than these small fluctuations is the average size of the shift in lifetime these variations could cause. To conservatively take into account this potential shift a 3% systematic error was added in quadrature with each lifetime determination. This is about three times the size of the error estimated by using the measured variations in detection efficiency. In nearly all cases, this 3% error totally dominates the overall error.

A potentially serious error is the possibility of confusing the desired decay channel with cascades through the path $B \rightarrow W \rightarrow B \rightarrow A$. The long estimated lifetime of the W state¹⁰ makes it very unlikely that this pathway could distort the apparent lifetime by much more than 1%. Nevertheless some simple experiments were performed to make sure that such distortion is not occurring. The first such experiment consisted of examining the decays of the $v=6$ and $v=7$ levels through interference filters that selected the 6–3 and 7–4 decay bands. Unfortunately, the accuracy of lifetime measurements made under these conditions is limited by a relatively large shift caused by angle tuning of the interference filter. As the molecules travel down the beam line the mean angle through the filter increases, and an increasing amount of the decay light is shifted outside of the filter passband. Apparent lifetime shifts in the range of 0%–8% are observed for various tipping angles of the filters. These shifts agree well with estimates based on the decrease in total signal size as the filters are tipped, but the estimates are not accurate to much better than 5%. Thus it can be concluded only that there is no evidence for effects on the $v=6$ and 7 lifetimes at the 5% level.

A second search for the effects of intrasystem cascading was made by looking for decay light through a filter that selected the 2–0 band of the first positive

TABLE II. Lifetimes of some rotational levels of the $v=6$ state.

J	τ (μ s)
2	5.54 \pm 0.24
3	5.60 \pm 0.25
4	5.30 \pm 0.17
5	5.38 \pm 0.18
7	5.35 \pm 0.26
8	5.41 \pm 0.19

system. Published A coefficients for the $B \rightarrow W$ and $W \rightarrow B$ decays¹⁰ suggest that most of the cascading would take place through B state levels with $v=0, 1$, and 2. The 2–0 band is the only one arising from these levels that can be observed with the 8852 photomultiplier. No evidence was found for laser-induced fluorescence on this band when the laser was tuned to the $v=6, 7$, and 10 levels, indicating that the cascade light on this band is present at a level no greater than 5% of the normal signal size. In addition, any distortion of the B state lifetimes is a second order effect, reduced both by the relative weakness of the cascade light and by the fact that fits to a single exponential are shifted only slightly by the presence of a component with a longer lifetime. The results of these two experiments indicate that intrasystem cascading has no significant effect on the lifetime measurements, although a contribution of up to 5% cannot be ruled out.

DISCUSSION

The lifetimes given in Table I include the 3% systematic error described in the previous section. An examination of the table shows that the results of the present measurement are in fairly close agreement with those of Jeunehomme, although the Jeunehomme results appear to be systematically too large by about 5%–10%. The agreement with Hollstein *et al.* is also good, although their results again indicate slightly longer lifetimes. The same cannot be said of the other existing measurements, which in general show very short lifetimes and weak or erratic vibrational variations. Since these measurements were made using methods similar to those of Jeunehomme,¹ it is not entirely clear why they disagree so strongly. Apparently the spectrum of higher excited states that can contribute cascade radiation after an unselective excitation pulse is somewhat richer than had been suspected.

Since the resolution of the laser system is easily sufficient to resolve the rotational structure, a brief search was made for rotational dependence of the lifetimes. Measurements of the $J'=2, 3, 4, 5, 7$, and 8 levels of the $v=6$ vibrational level are summarized in Table II; they show no significant variation. This is in accord with the observation of Dieke and Heath⁹ that the B state is nearly free from perturbations with neighboring states.

The only theoretical calculation of the B state lifetimes is in an article by Breene,¹¹ and is apparently not of sufficient accuracy to constitute a real test of the ex-

perimental values. Transition moments for the first positive system have been calculated both from the results of Jeunehomme¹ and from an approach by Shemansky and Broadfoot⁵ that combines relative intensity measurements with a single lifetime measurement. The accurate lifetimes given here largely confirm the accuracy of these transition moments, since the lifetime measurements are in excellent agreement with Jeunehomme's measurements to within 10%. The much weaker variation with the vibrational level indicated by most of the recent lifetime measurements can be ruled out.

The extremely high resolution and good signal to noise ratio seen in this experiment suggest that the experimental technique could easily be applied to other problems. Many atoms and diatomic molecules have highly excited metastable states that are within 1 or 2 optical photon energies of the ionization limit. This raises the exciting prospect that the structure and lifetimes of high Rydberg states can be examined with high precision in systems that were previously almost inaccessible. Efforts are presently underway to pursue some of these possibilities.

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